



Project Summary

Speciation of Selenium in Groundwater

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A study was conducted to investigate ion chromatography (IC) for determining selenium species in groundwaters. Analytical speciation of selenium was investigated because the removal efficiencies of various processes for selenium removal (activated alumina in particular) depend on which species (Se IV or Se VI) is predominant in the groundwaters.

In addition to investigating IC, the study aimed at determining a preservation technique for maintaining species integrity and at analyzing field samples taken from seleniferous regions to assess which of the two selenium species predominates.

Results showed that IC is suitable for selenium (VI) analysis in groundwater samples if the sample is pretreated with a $\text{Ba}(\text{OH})_2$ dose to remove the sulfate interference. The selenium (IV) concentration can then be determined as the difference between the total selenium concentration (as determined by furnace atomic absorption spectroscopy) and the selenium (VI) value as determined by IC. The detection limit for selenium (VI) in groundwater samples treated with $\text{Ba}(\text{OH})_2$ is approximately 0.020 mg/L. IC should therefore determine the predominant selenium species in a groundwater if the total selenium concentration is above 0.050 mg/L.

The analysis of field samples did not conclusively determine the predominant selenium species because only 30% of the collected samples had total selenium values above 0.050 mg/L. Neither species predominated in the samples that were analyzed.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce

key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The total selenium concentration in potable water is Federally regulated not to exceed 0.01 mg/L because of potential health effects. Many groundwater supplies in seleniferous areas of the country such as South Dakota, Colorado, Oklahoma, Kansas, Wyoming, and southern California contain selenium levels considerably above the Federal limit. An effective removal technology is required if these drinking water supplies are to meet the standard.

Activated alumina was investigated as a selenium removal technique in earlier studies sponsored by EPA, but its removal efficiency depends on the selenium species present. Alumina effectively removed selenium in the +IV valence state (selenite) but not in the +VI valence state (selenate). The difference is due to the lower absorption affinity of Se(VI) and its greater susceptibility to interferences from other anions. Earlier investigations of other treatment processes, including coagulation with alum or ferric sulfate, revealed the same poor removal of Se(VI). Ion exchange preferentially removes sulfate over Se(IV) and removes sulfate and Se(VI) equally. Reverse osmosis is effective for removing both species of selenium, but the operational cost is too high for routine applications.

The predominant selenium species in groundwater supplies is not well characterized because the element is regulated as total selenium, and the EPA-approved analysis method is atomic absorption spectroscopy (AAS), which

cannot differentiate between species. Determination of the predominant selenium species in groundwater supplies containing significant amounts of selenium is needed to assess the feasibility of selenium removal by activated alumina.

There is a vast range of documented methodologies for determining Se (IV), but none of the procedures are straightforward. All require organic solvent extractions or preconcentration schemes to lower the detection limit. Furthermore, none of these methods is capable of direct determination of Se (VI), which can only be determined by the difference between Se (IV) and total selenium concentrations. The IC technique is rapid and simple, requires no sample pretreatment that could alter speciation, and is capable of detecting both selenium species simultaneously. Refinement of the method is required, however, to achieve adequate sensitivity to detect selenium species at the $\mu\text{g/L}$ level and to eliminate interferences from other anions.

This study evaluates IC as an analytical method for determining selenium species in groundwaters. Optimization of instrumental sensitivity and selectivity for the selenium species was investigated by varying instrumental parameters and, if required, establishing initial pretreatment schemes to eliminate interferences. Sample preservation techniques were also investigated to develop a scheme that would preserve the integrity of the selenium species. Finally, selected groundwater samples from seleniferous regions were analyzed to determine which selenium species, if any, predominates in the environment.

Materials and Methods

The IC used in this study was a Dionex Model 16* with conductivity detection. Hardcopy output was collected on a Pederson recorder, and peak quantification was performed manually by measuring peak heights. Peak heights were measured manually rather than by computerized peak integrations because of the difficulty in setting adequate integration baselines for poorly resolved peaks. Table 1 lists the standard instrumental operating conditions and columns that were used.

Selenite and selenate standards of 25 and 50 $\mu\text{g/L}$ were analyzed by IC under standard operating conditions to determine retention times and

Table 1. Standard Instrumental Operating Conditions

Instrument Parameter	Operating Condition
Columns	4- x 5-mm Fast-Run (AS3) Pre-Column (P/N 030831) 4- x 250-mm Fast-Run (AS3) Separator Column (P/N 030831) Fiber Suppressor Column (P/N 35350)
Eluent	0.003 M NaHCO_3 /0.0024 M Na_2CO_3
Eluent Flow Rate	2.07 mL/min
Sample Loop Size	600 μL
Detector Sensitivity	0.3 μmho /full scale
Recorder Sensitivity	100 mV/full scale

sensitivities. A mixed 25 $\mu\text{g/L}$ selenite, 25 $\mu\text{g/L}$ selenate standard was made up fresh each analysis day and run by IC to determine any any significant change in peak height for either species. The peak height values obtained for the selenite and selenate standards over the duration of the project were recorded.

Due to slight instrument variations, the peak heights for the selenite and selenate changed slightly from day to day. Evidence of contamination or degeneration of a stock would appear as a steadily increasing or decreasing peak height value more than 2σ away from the mean. No such evidence was observed during the duration of the project.

The selenite and selenate stock standards were prepared with reagent grade Na_2SeO_3 and Na_2SeO_4 and initially verified by graphite furnace AAS. The barium hydroxide used in sample pretreatment and the tested preservatives were all reagent grade.

Resolution Study

Table 2 presents retention times, instrumental sensitivities, and detection limits for selenite, selenate, and some of the common anions that should be present in groundwaters at significant levels. The selenite and selenate detection limits of 8 $\mu\text{g/L}$ in deionized water are only marginally acceptable in light of EPA's current maximum contaminant level (MCL) of 0.01 mg/L for total selenium, but investigation of concentration methods such as column loading could lead to adequate detection limits.

Most groundwaters containing selenium levels above 10 $\mu\text{g/L}$ also contain sulfate levels ranging from 100 to 1000 mg/L. This indicates a probable interference problem between the selenate and sulfate peaks, which was verified by running mixed selenate-

sulfate standards. A 10- $\mu\text{g/L}$ selenate and 100-mg/L sulfate standard produced a detectable selenate peak, but resolution was too poor for reliable quantification. A similar interference problem was observed for selenite in the presence of chloride.

Instrumental parameters were varied as a means of achieving adequate resolution between the selenate and sulfate peaks. To increase column efficiency, the eluent flow rate was reduced from 2.1 mL/min to 1.3 mL/min, but this had no effect on resolution. Use of two AS3 separator columns connected in series to increase column capacity also had no impact on resolution. Use of a weaker eluent to improve resolution was not investigated because the selenate and sulfate are such similar species that they both would be affected to the same degree.

Chemical pretreatment, by adding $\text{Ba}(\text{OH})_2$, was investigated as a means to eliminate the sulfate interference. Adding a barium salt should precipitate sulfate without precipitating selenate because of the much lower solubility product of BaSO_4 and the much lower concentration of selenate in groundwaters. To empirically test the efficacy of barium addition, a set of selenate-sulfate standards were analyzed with and without the added barium. Stoichiometric addition of barium to match the sulfate concentration effectively improved resolution between a 25 $\mu\text{g/L}$ selenate and 100 mg/L sulfate standard to the point where the selenate could be quantified. Barium addition in excess of the sulfate concentration resulted in loss of some of the selenate; this indicates that barium addition is effective only when the dose is stoichiometrically matched to the sulfate concentration. The speciation was not altered after barium,

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 2. Retention Times, Sensitivities, and Detection Limits for Selenite, Selenate, and Other Common Anions

Anion	Retention Time (minutes)	Sensitivity ($\mu\text{mho/ppb}$)	Detection Limit (ppb)
Selenite	4.6	0.0013	8
Selenate	11.8	0.0013	8
Chloride	2.4	0.012	1
Nitrate	6.6	0.012	1
Sulfate	8.4	0.002	5

as hydroxide, was added to a mixed selenite-selenate standard and the pH increased from 6 to 12.

Preservation Study

The optimum preservation method for maintaining selenium speciation is not known. Numerous studies have been published but the results are contradictory; many studies used unrealistically high selenium species concentrations that were orders of magnitude above those found in the environment. A preservation study was run to find an adequate method to maintain speciation—one that wouldn't interfere with the IC analysis.

Mixed selenite-selenate standards (25 $\mu\text{g/L}$ each) were stored in 125-mL and 500-mL glass and polyethylene containers. A variety of preservatives were added and monitored for a 3-week period: reducing agents were tested to see whether they would prevent oxidation of selenite to selenate because groundwater samples originate from a much more anoxic environment; although pH reduction could cause species conversion, it was evaluated because it is the standard preservation technique for total selenium; a biological inhibitor was investigated to determine whether biological activity in a field sample could be removing selenite or selenate.

Perchloric acid addition was eliminated because the perchlorate peak overshadowed both the selenate and selenite peaks. The integrity of the mixed selenite-selenate standards was maintained over the 3-week period for all of the preservation conditions except for nitric acid addition, which converted all the selenate to selenite.

Field Sample Data

Twenty-one field samples from Kansas, South Dakota, Colorado, and Oklahoma were received. Since all the preservation methods appeared comparable, the field samples were collected in polyethylene containers. An aliquot was transferred to

a 60-mL polyethylene bottle and acidified to a pH <2 with nitric acid for total selenium analysis by graphite furnace AAS. The remainder of the sample was refrigerated before analysis and then analyzed for pH, alkalinity, sulfate, chloride, selenate, and selenite (Table 3).

The analytical results are given in Table 4. The total selenium concentrations in these samples ranged from 620 $\mu\text{g/L}$ to <1 $\mu\text{g/L}$, but 60% of the samples were below 20 $\mu\text{g/L}$ and 70% were below 50 $\mu\text{g/L}$. Only 8 of the 21 samples had total selenium concentrations high enough to be detected by ion chromatography. Only one of these eight samples gave a resolvable peak for selenite as well as selenate. The summation of the selenite and selenate concentrations obtained by IC (141 $\mu\text{g/L}$) was in excellent agreement with the total selenium value of 150 $\mu\text{g/L}$ obtained by graphite furnace AAS. Selenate was detected in two other samples, but selenite could only be determined as the difference in value between the total selenium and selenate since the chloride peak interfered. Selenate was not detected in the remaining samples because the concentration was probably below the matrix detection limit. In the three samples containing selenate/selenite, the distribution was 50% selenate/50% selenite for two samples and 70% selenite/30% selenate for the third.

Conclusions and Recommendation

IC with conductivity detection lacks sufficient sensitivity and resolution to

determine selenite and selenate at levels near the current EPA MCL of 0.01 mg/L. Although the instrument detection limit is 8 $\mu\text{g/L}$ for each species, the matrix detection limit is higher because of interferences from sulfate and chloride.

Dosing samples with $\text{Ba}(\text{OH})_2$ stoichiometrically matched to the sulfate concentration effectively removes the sulfate interference and allows quantification of selenate, but the selenate-matrix-dependent detection limit is somewhere between 15 and 25 $\mu\text{g/L}$.

Addition of ion-exchange resin in silver form to remove chloride interference when detecting selenite was not investigated in this study but should work effectively.

Except for nitric acid, which immediately converted selenate to selenite, all preservation methods appeared adequate over a 3-week holding period.

70% of the field samples had total selenium values below 50 $\mu\text{g/L}$ and could not be analyzed successfully for speciation by IC. Of the few samples analyzed by IC and AAS, the agreement was good.

Analytical modifications that might improve the current detection limit so that low levels of selenium could be speciated are the use of: off line loading of a concentrator column; IC to achieve species separation with subsequent detection by graphite furnace AAS; recycle chromatography; or UV detection instead of conductivity detection IC.

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Table 3. Analytical Methods Used in Analysis of Field Samples

Analysis	Method Ref.	Description
Alkalinity	EPA 310.1	Manual Titration
Chloride	EPA 325.2	Automated Ferricyanide
pH	EPA 150.1	Electrode
Sulfate	EPA 375.2	Methylthymol Blue
Total Selenium	EPA 270.2	Graphite Furnace AAS
Selenium Species	————	Ion Chromatography

Table 4. Analytical Results for Field Samples

Sample Name	Total Selenium (µg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alkalinity (mg/L CaCO ₃)	pH (Units)	Se(VI) (µg/L)	Se(IV) (µg/L)
A(KS) ^a	150	440	19	270	7.7	35	106
B(KS)	80	200	37	230	7.9	44	ND ^b
C(KS)	30	129	57	270	7.7	ND	ND
D(KS)	60	320	119	320	7.3	ND	ND
E(KS)	10	133	25	40	7.4	NA	NA
F(KS)	< 1	172	482	240	7.9	NA	NA
G(KS)	16	480	18	300	7.6	ND	ND
H(KS)	12	79	28	290	7.8	NA	NA
I(CO)	620	990	191	290	7.6	342	ND
J(CO)	60	485	110	310	7.4	NA	NA
K(CO)	19	168	49	320	7.9	NA	NA
L(CO)	10	166	61	165	--- ^c	NA	NA
M(CO)	17	173	58	280	7.8	NA	NA
N(CO)	10	178	46	220	7.9	NA	NA
O(CO)	15	162	65	220	7.7	NA	NA
P(OK)	10	77	165	250	8.0	NA	NA
Q(OK)	17	53	5.9	320	8.8	NA	NA
R(OK)	8	81	95	340	7.6	NA	NA
S(OK)	70	145	160	380	7.7	NA	NA
T(SD)	19	177	11	320	7.9	NA	NA
U(SD) ^d	30	870	254	210	7.7	NA	NA

^a KS = Kansas

CO = Colorado

OK = Oklahoma

SD = South Dakota

^b ND = Not Detected

NA = Not Analyzed

^c Insufficient sample for analysis

^d Traces of chlorine in raw sample

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Richard Lauch is the EPA Project Officer (see below).

The complete report, entitled "Speciation of Selenium in Groundwater," (Order No. PB 85-125 979; Cost: \$8.50, subject to change) will be available only from:

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